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BNL-77650-2007-JA

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Accepted for Publication in IEEE Transaction on Applied Superconductivity (2007)

February 26, 2007

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Effects of Reaction Temperature and Alloying on Performance of Restack-rod-process Nb_3Sn

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***Abstract*—Final reactions of 48 or 50 hours were given in a range of temperature from 635 °C to 695 °C to high-J_c Ta- and Ti-alloyed Restack-Rod-Process Nb_3Sn strands to investigate the changes in critical current density J_c and the superconducting properties. J_c is the current density in the non-copper region of the wire. Measurements of J_c were made at 4.2 K temperature and from 8 to 11.5 T field at BNL and from 12 to 16 T at OST, and these data were fitted to the Summers expression for J_c to extrapolate the scaling field B_{c2}*. All three $(Nb,Ta)_3Sn$ strand designs investigated displayed peak J_c values of ~3000 A/mm^2 at 12 T and ~1500 A/mm^2 at 15 T for 665 and 680 °C reactions. B_{c2}* increased monotonically with increasing reaction temperature. By comparison, at each reaction temperature, a $(Nb,Ti)_3Sn$ strand under development had a higher B_{c2}* than any of the Ta-alloyed strands. This suggests that Ti-alloyed strands could improve high-field performance if further development can bring their J_c values closer to those of the Ta-alloyed strands. Other implications are also discussed.**

***Index Terms*—Electric variables measurements, niobium-tin compounds, heat treatments, superconducting filaments and wires**

I. Introduction

THE next generation particle accelerator for high energy physics (HEP) beyond the Large Hadron Collider (LHC) will require high field superconducting magnets that move well beyond Nb-Ti technology. One of the possible scenarios of a future upgrade of LHC in terms of its luminosity, which is being studied by the LHC Accelerator Research Program (LARP), is to replace the interaction region quadrupoles with higher field-gradient magnets than the current Nb-Ti quadrupoles. These high gradient quadrupoles could operate at 12-16 T, which requires Nb_3Sn conductor with high critical current density J_c.

At present the highest J_c, >3000 A/mm^2 within the non-copper region of the wire at 12 T and 4.2 K, has been achieved by Oxford Instruments, Superconducting Technology (OST) in internal-Sn strand designs using the Restack-Rod Process (RRP) [1]. Sub-elements with Nb alloy filaments in a copper matrix and a Sn alloy core are restacked in this process. The Nb alloy content is maximized by minimizing the copper fraction while also providing enough Sn for complete conversion to Nb_3Sn. During reaction, the small filaments expand and merge together to act as a single effective filament per sub-element. As a result of minimizing the copper content, the bronze has high tin content, which accelerates the growth of Nb_3Sn. This promotes full reactions while retaining fine grain size for final reaction times of ~48 hours. In addition, each sub-element is surrounded by a Nb barrier which also partially converts to Nb_3Sn and contributes to the J_c.

Nearly all commercial Nb_3Sn strands are ternary alloys with either Ta or Ti to enhance the upper critical field B_{c2}. Most of the RRP wires produced by OST use Nb7.5wt%Ta alloy rods to form $(Nb,Ta)_3Sn$. This is a well-established process that achieves the J_c of ~3000 A/mm^2 indicated earlier. In a new process [2], pure Nb rods are combined with a small number of Nb47wt%Ti rods, using the relatively cheap and widely available standard alloy for Nb-Ti wires. This mixture of Nb and Nb47wt%Ti filaments react to form $(Nb,Ti)_3Sn$. Ti-alloyed RRP composites with 91 or 127 sub-elements have been fabricated by OST, which attain J_c > 2400 A/mm^2 at 12 T at this stage of development [3].

For RRP wires in general, the filament diameter is effectively the sub-element diameter, which in a 0.7 mm wire with 54 sub-elements and 50% stabilizing copper is ~70 μm. The combination of large effective filament diameters and high J_c makes strands susceptible to flux jumps at low fields. This magnetic instability can prevent wires from carrying transport currents. By measuring the voltage in a wire carrying a fixed current while the field is swept between 0 and 4 T, it is possible to determine a stability current density J_s, above which flux-jumps can quench the wire [4]. In a study of RRP wires [5], it was found that J_s was correlated with the strand residual resistance ratio *RRR*. A low *RRR* of 5 to 10 dropped J_s below J_c at 12 T, which in a magnet would limit its performance due to quenching in the low field sections. The low *RRR* results from tin diffusion through the Nb barrier and into the copper matrix. Hence, the strand stability, as well as its performance, is dependent on the reaction temperature and time.

In this paper we report on critical current measurements of 0.7 mm diameter wires from three RRP $(Nb,Ta)_3Sn$ billets (8220, 8647 and 8648) and one $(Nb,Ti)_3Sn$ billet (8079), that were produced for the Conductor Development Program (CDP) [6]. The results explore the influence of the reaction temperature and time on J_c, *RRR* and the extrapolated upper

Manuscript received August 28, 2006. This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

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temperature and time on J_c, *RRR* and the extrapolated upper critical field B_{c2}*, which is defined in section II-*B*. The $(Nb,Ta)_3Sn$ billets consist of 54 sub-elements with a non-Cu fraction of 0.52. The $(Nb,Ti)_3Sn$ billet has 90 sub-elements with a non-Cu fraction of 0.59. In the finished wire, the sub-element diameters for $(Nb,Ta)_3Sn$ billets are ~ 69 μm, whereas for the $(Nb,Ti)_3Sn$ billet it is ~ 60 μm.

II. Measurements and Procedures

A. Heat Treatments and Wire I_c Measurements

Wire samples from the different billets were reacted using intermediate temperatures of 210C/48h + 400C/48h, followed by a variety of final reaction temperatures and times. These were reacted on either stainless-steel barrels (BNL) or Ti-Al-V alloy barrels (OST) and then transferred to the test barrels.

The critical current, I_c, at 4.2 K was measured as a function of field by recording the voltage V across a length of specimen (50-100 cm) as a function of increasing current. I_c is defined as the current at which the sample resistivity is 10^{-14} Ω-m, as is usual defined for Nb-Ti wires. The facility at Brookhaven National Laboratory (BNL) used a variant of the ITER-holder [7] more suited for high current testing. The sample heat-treatment, assembly and test procedures, described in [8], routinely permit testing of high-J_c wires to a maximum field of 11.5 T and a maximum current of 1.5 kA. The measurements at OST were done in the field range of 12-16 T (outside the range of BNL measurements) using similar sample holders.

*B. Data Fitting and B_{c2}**

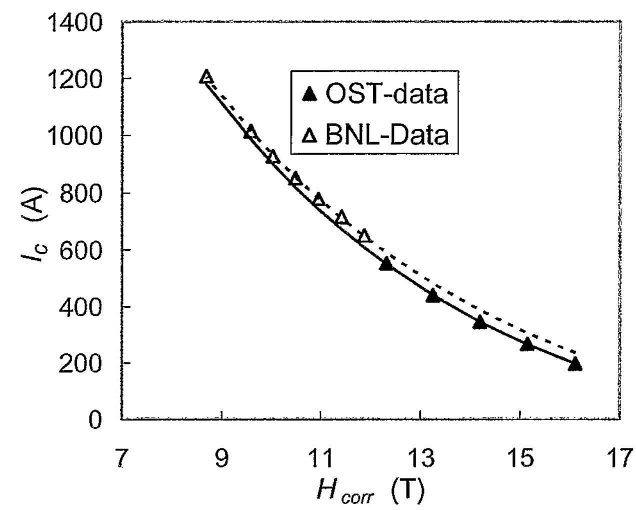

Fig. 1. I_c as a function of H_{corr}.

The raw I_c data compared between the two labs did not have exactly the same $I_c(H)$ behavior. Part of the problem stems from the fact that the critical currents at 8-10 T are ~1000 A, which distorts the $I_c(H)$ behavior due to the self-field generated by these high currents. Hence a first step to properly compare data over a large field range is to correct for the self-field [9]. The corrected field is given by (1).

$$H_{corr} = H + (4\times10^{-4})I_c d^{-1} \qquad (1)$$

Here H is the applied field in A m^{-1}, H_{corr} is the corrected field, and d is the wire diameter in mm.

In addition to the self-field correction, the strain dependence of I_c for Nb_3Sn wires contributes to variations between different test stations. All else being the same, a wire in different test holders can be in slightly different strain states at 4.2 K. For example, in Fig. 1, the I_c measured at BNL and at OST for this wire is plotted as a function of H_{corr}. The 12-16 T OST data are fitted (solid line) using the Summers formulation [10] with a typical strain:

$$J_c = C(e)B_{c2}^*(T,\varepsilon)^{1/2}(1-t^2)^2 b^{-1/2}(1-b)^2 \qquad (2)$$

Here $b=B/B^*_{c2}(T,\varepsilon)$, $B^*_{c2}(T,\varepsilon)$ is the upper critical field, expressed with its temperature T and strain ε dependence, B is the applied field, $t=T/T_{c0}(\varepsilon)$, $T_{c0}(\varepsilon)$ is the critical temperature in zero field, and C is a strain dependent scaling coefficient. The following parameters were used: strain $\varepsilon = -0.003$, $B_{c20} = 27.7$ T, and $T_{c0} = 17.8$ K. In this formulation $B^*_{c2}(T,\varepsilon)$ abbreviated here as B_{c2}* is the same as $\mu_0 H_K$ using the Kramer extrapolation as used in other work [11]. (Note that in the Summers formulation the upper critical field and the scaling field for flux pinning are the same, which does not take into account very recent discussion [12],[13]. By only changing ε by -0.0005 and keeping all other parameters fixed, the BNL data can be properly fitted as shown by the dashed line in Fig. 1. This is consistent with the different groove designs of the BNL and OST test barrels, which lead to slightly different strain at 4.2 K. The difference in I_c at 12 T is ~5%.

III. Measurement Results

A. J_c Optimization at 12 T

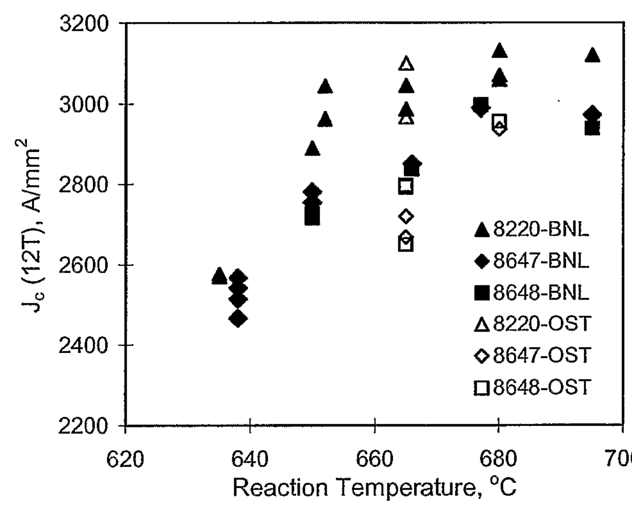

Fig. 2. J_c at 12 T of RRP billets versus the final reaction temperature. Closed symbols are for BNL data, and open symbols for OST data.

Fig. 2 is a plot of the J_c at 12 T versus final reaction temperature, with reaction duration limited to 48 or 50 hours. For the BNL data, no correction is made for self-field prior to extrapolating to 12T. Very good performance is generally seen for all strands, with 8220 exceeding 3100 A/mm^2 and all strands exceeding 2900 A/mm^2 in a window of reaction temperature from 650 to 695 °C. As discussed in more detail later, the ability to attain good performance at lower reaction temperatures (650 and 665 °C) is important for HEP magnets operating in the range of 11-12 T, because not only the J_c(12 T) but also the *RRR* must be optimized so that the stability current J_s is considerably higher than J_c.

In comparing the three billets, billet 8220 has a higher J_c than 8647 and 8648 when given a 665 °C reaction for 48 hrs. A J_c comparable to that of 8220 is observed for 8647 and 8648 when reacted at higher temperatures or for longer times, e.g. 96 hrs at 665 °C (not shown). The likely reason for this difference is slight variations in the sub-element billet material. In all cases, the J_c is highest for 48 h reactions of 665 or 680 °C and falls off for higher temperatures. The scatter in J_c values for a given billet at a specific reaction temperature is more likely due to variations in sample testing conditions (strain, in particular) rather than variations within the billet itself.

How does *RRR* vary with reaction temperature and time? Fig. 3 is a plot of the $(Nb,Ta)_3Sn$ billets measured at BNL and OST. In the temperature range of 635-665 °C, *RRR* changes slowly, and measurements of J_s show that it exceeds 5000 A/mm^2. However at higher temperatures, >680 °C, both J_s and *RRR* drops more sharply [14], indicating that more Sn diffuses through the barrier and contaminates the copper. A similar change is observed at 665 °C by increasing the duration of reaction from 50 to 100 hrs. Based on these data, we find that reactions at 665 °C for 48 hr is best for the 2-parameter optimization (J_c(12 T) and *RRR*) for HEP magnets using these strands.

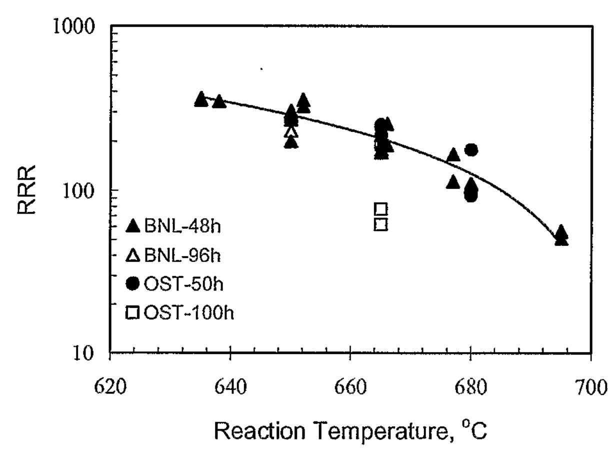

Fig. 3. Plot of *RRR* as a function of reaction time and temperature for 8220, 8647 and 8648. The solid line is a trend line for reactions of 48-50 hrs.

B. Optimization of J_c at 15 T

Whereas it is important to optimize both J_c and *RRR* for magnets operating at 11-12 T, optimizing for magnets operating in the 15-16 T range requires a slightly different approach. In this case, the slope of the $J_c(H)$ curve, which is parameterized by $B_{c2}*$, is of more importance. *RRR* is not, since J_s is still >2000 A/mm^2 even when *RRR* falls to ~10, and is also higher than J_c at 15-16 T. It is thus possible to utilize aggressive reactions to maximize J_c at 15 T. In Fig. 4, the J_c of the wires measured at 15 T at OST are plotted for reaction times ranging from 50 to 100 hrs. The best data for 8220 show J_c exceeding 1600 A/mm^2. For billets 8647 and 8648, J_c(15 T) of > 1500 A/mm^2 is obtained by increasing the reaction time at 665 °C from 50 to 100 hrs. This again points to the fact that Sn diffusion in 8647/8648 is slower than that in 8220.

These results show that for 15 T, the optimal reaction temperature is 680 °C. As we shall see in the next section, at the higher reaction temperatures the $J_c(H)$ curve is less steep than at lower temperatures, resulting in higher J_c in the 15-16 T range.

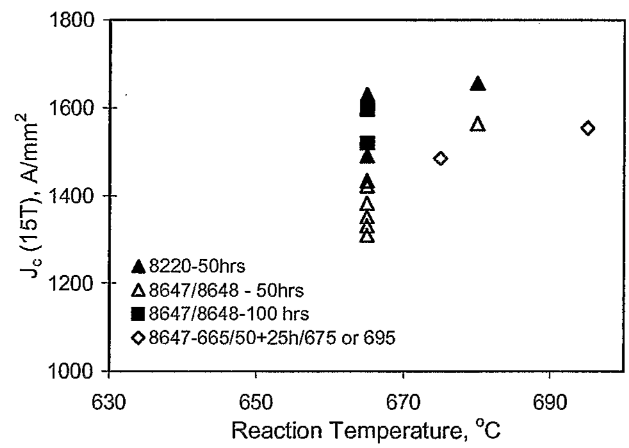

Fig. 4. J_c at 15 T, 4.2 K for the RRP-$(Nb,Ta)_3Sn$ billets, 8220, 8647 and 8648.

C. $B_{c2}*$ Optimization for J_c at 15 T

Since the measurements at BNL extend to only 11.5 T, the I_c at 12 T is obtained by fitting the data to the Summers equation (2) and extrapolating to 12 T. The main parameter that one obtains from the fit is $B_{c2}*$, which characterizes the slope of the $J_c(H)$ curve. However, as shown in section II, to get a meaningful value for this parameter, self-field corrections are needed.

In previous studies of MJR (Modified Jelly-Roll process) strands, I_c measurements in the range of 16-23 T were used to show that Ti additions to binary Nb_3Sn composites or ternary $(Nb,Ta)_3Sn$ composites gave a higher extrapolated $B_{c2}*$. The highest fields were obtained for quaternary $(Nb,Ta,Ti)_3Sn$ composites [15].

Fig. 5 is a plot of $B_{c2}*$ extracted from the measurements at BNL of wires from billets 8820, 8647, 8648 and 8079, where the applied field is corrected by using Eq. (1). It shows that $B_{c2}*$ increases monotonically for the Ta-ternary billets in the range of temperatures studied. For the Ti-ternary 8079, $B_{c2}*$ is always higher than the Ta-ternary, and it seems to be saturating at the higher temperatures. In addition, extending the reaction time at 650 °C from 48 to 96 and finally to 144 hrs for the Ti-ternary not only increases J_c from 2580 to 2800 A/mm^2, it also increases B_{c2}*. In contrast, at 650 °C, the Ta-ternary shows very little change in B_{c2}* between 48 to 96 hrs.

Fig. 6 is a plot of B_{c2}* for the OST data also corrected for self-field. Again we observe that the B_{c2}* trends are similar for the Ta-ternary and the Ti-ternary. Data for a recent CDP billet 8720 which is a (Nb,Ti)$_3$Sn composite with sub-elements that have higher Nb and Sn content than 8079 is also included in the plot. It attains a J_c of 2750 A/mm^2 at 12 T for a 50 hr final reaction at 665 °C. Wires from this promising billet are being investigated further.

Thus, these data suggest two strategies for 15 T applications: reactions at higher temperature, e.g. 680 °C for 48 hrs, and alloying with Ti.

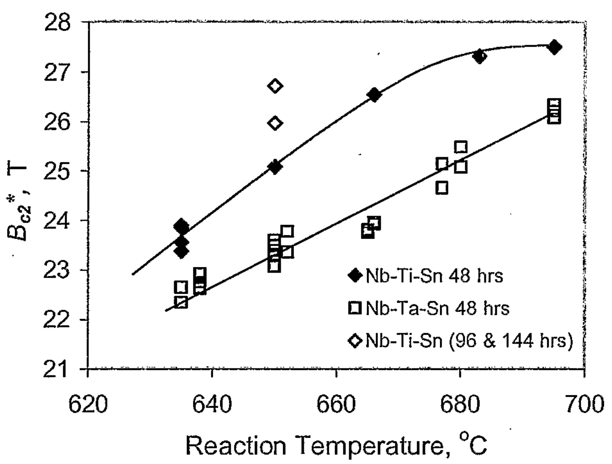

Fig. 5. B_{c2}* as a function of reaction temperature for (Nb,Ta)$_3$Sn and (Nb,Ti)$_3$Sn composites, BNL measurements. Lines are drawn to highlight the trend.

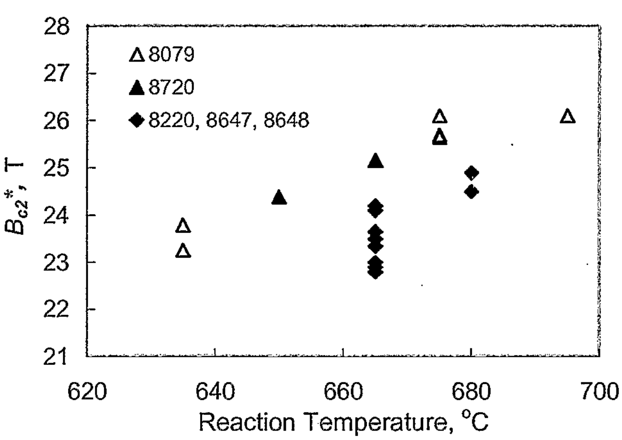

Fig. 6. B_{c2}* as a function of reaction temperature for (Nb,Ta)$_3$Sn billets 8220,8647 and 8648, and for the (Nb-Ti)Sn billets 8079 and 8720, OST data.

IV. Summary

These experiments show that there is a fair amount of flexibility for tuning J_c and *RRR* by adjusting the reaction temperature and time. For magnet application in the 11-12 T range, (Nb,Ta)$_3$Sn composites like 8220 can readily be optimized by limiting the reaction temperature to 665 °C for 50 hrs. This ensures that the *RRR* is still high enough to provide adequate stability at low fields, while also attaining J_c > 3000 A/mm^2. However, for higher field magnets in the 15-16 T range, results of this study show that higher reaction temperatures improve the J_c at 15 T. The penalty of lower *RRR* is not as important, since the ~2000 A/mm^2 stability current density is considerably higher than the 15 T J_c of ~ 1500 A/mm^2 even for *RRR* of ~10. Ti alloying is, furthermore, very promising for additional improvement beyond present Ta-alloyed billets, and could result in J_c (15 T) in excess of 1600 A/mm^2 with continued development.

Acknowledgment

The authors from BNL thank J. D'Ambra for heat treating and the mechanical assembly of the samples, and E. Sperry for his expert help in measuring the critical current of the strands.

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